OST TECHNICAL PROGRESS REPORT
TEAM WORK PLAN -- FY 2001 RESULTS

TITLE: $PM_{2.5}$ Site Sampling and Analysis Team

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DESCRIPTION: The NETL-OST in-house $PM_{2.5}$ Site Sampling and Analysis program performs in-depth research to characterize ambient air concentrations of particulate matter with an aerodynamic diameter of 2.5 micrometers or less ($PM_{2.5}$). In particular, this research program is directed toward determining the method and degree by which fossil-fuel-fired electric power generating stations contribute to the primary particulate matter load in ambient air. This program will develop high-quality scientific information for decision makers to implement effective, cost-efficient strategies to meet the stringent, revised, National Ambient Air Quality Standards (NAAQS) of 1997.

RESEARCH OBJECTIVES: The research objective for FY 2001 consisted of the following program activities:

> Complete NETL's on-line air quality monitoring network to provide comprehensive ambient air monitoring data, including total particulate size distribution and $PM_{2.5}$, carbon composition, nitrate/sulfate particulate analysis, state-of-the-art characterization of organic components, and gas phase contaminant concentrations.

LONG TERM GOALS / RELATIONSHIP TO NETL'S PRODUCT LINES:

> Provide independent data to assess the contributions of coal-fired power to primary and secondary $PM_{2.5}$ to supplement a nationwide ambient monitoring network through 2003 and subsequent decision making by EPA and state regulators during 2002-2008 for regions that are not in compliance with the new NAAQS $PM_{2.5}$ 24-hr average limit of 65 ug/m^3 and annual mean limit of 15 ug/m^3.
>
> Evaluate $PM_{2.5}$ along with interrelated factors, including NO_x, SO_2, NH_3 slip, unburned carbon, Hg, and other hazardous air pollutants (HAP), that could impact future technology choices for coal-fired utilities located in states that will be required to submit implementation plans by 2008, with full compliance with the NAAQS by 2017.

"The overall goal of the DOE-FE fine-particulate program is to ensure that the best science and technology is available for any regulatory-decision making related to the health and environmental impacts of ambient fine-particulate matter and regional haze."[1] The NETL/OST $PM_{2.5}$ Site Sampling and Analysis program directly supports this goal in the interest of the Environmental and Water Resources Product Team.

ACCOMPLISHMENTS: The research accomplishments of the $PM_{2.5}$ Site Sampling and

Analysis Team in FY 2001 are summarized below:

The second full year of successful operation of a state-of-the-art ambient-air fine-particulate monitoring station with comprehensive analytical capabilities at NETL has been completed. This station, initially constructed in FY99, is part of a network of air sampling stations that together constitute the UORVP. The NETL air monitoring station consists of a 715-ft^2 indoor facility housing equipment to continuously monitor the gaseous pollutants O_3, SO_2, CO, NO_X, NO_Y, NH_3, and H_2S, as well as $PM_{2.5}$ particles containing carbon and polycyclic aromatic hydrocarbons (PAH).

NETL - PM $_{2.5}$ Ambient Air Monitoring Station

NETL-$PM_{2.5}$ Instrument Rack

In addition, a fully-instrumented, fourteen-bay rack supports a variety of $PM_{2.5}$ monitoring equipment. The specific location of the sampling station was chosen to take full advantage of the existing meteorological tower to supply full weather data for the program, including temperature, humidity, UV intensity, rainfall, barometric pressure, wind speed, and wind direction. The fine-particulate monitors collect filter-based samples so that the mass of the particles can be determined by weighing in the MSHA world-class balance room in a building adjacent to the air monitoring station. The site is also host to a sampling system developed at BYU that samples both particulate matter and semi-volatile organic compounds in the vapor state.

The list of specific monitoring equipment at NETL's ambient air monitoring station includes:
$PM_{2.5}$ Partisol®- Plus FRM Sequential Air Sampler (R&P),
ENVIROcheck Model 107M Environmental Particulate Monitoring System (Grimm),
$PM_{2.5}$ DustTrack Aerosol Monitor (TSI),
$PM_{2.5}$ TEOM® Ambient Particulate Monitor equipped with an AccuSampler (R&P),
$PM_{2.5}$ RASS 2.5-400 Speciation Sampler (Andersen),
PAS 2000 Real-time PAH Monitor (EcoChem Analytics),
Seven Day Pollen and Mold Spore Trap (Burkard),
Continuous Gas Monitors -- SO_2, O_3, CO, NO_X, NO_Y, NH_3, H_2S (API) and Peroxide (Kok),
$PM_{2.5}$ PC-BOSS Sampler (BYU),
High Volume Samplers (BYU and NETL),
$PM_{2.5}$ Ambient Carbon Particulate Monitor (R&P),
Highly Instrumented Meteorological Tower (Climatronics),

$PM_{2.5}$ Continuous Nitrate Analyzer (R&P),
ELPI™ particle size distribution and concentration measurement system (Dekati),
$PM_{2.5}$ Seven-channel Aethalometer (Andersen), and
$PM_{2.5}$ Continuous Sulfate Analyzer (R&P).

RESULTS:

Continuous and batch air monitoring program

Continuous analyzers to measure particle size and particulate nitrate and sulfate content were purchased and deployed in FY01. These analyzers complete the suite of continuous instrumentation located at NETL to characterize ambient fine-particles in real-time, supplementing and replacing some of the labor intensive batch collection techniques often used to speciate ambient fine-particulate matter. Results summarizing a year of continuous particulate measurements in FY00 are being published in a peer-reviewed journal article [2] with the FY01 results targeted for a similar extensive article to be prepared in FY02.

An in-depth article containing results of both continuous and batch sample speciation characterization was prepared in FY02 to be published in Energy and Fuels in March of 2001[3]. This article relates the measured abundance and composition of $PM_{2.5}$ at the NETL site to meteorological transport from sources in the upper Ohio River valley basin. Figure 1, which was included in the published findings, illustrates the directional pattern of $PM_{2.5}$ high concentration episodes to the origin of the air mass transporting the particles to the NETL site.

A more comprehensive article covering a greater time period and containing particulate concentration data from continuous analyzers located thoughout the upper Ohio River valley is in preparation[4].

Characterization of the organic components of $PM_{2.5}$ particles

In FY01, NETL researchers refined the methodology to analyze for the semi-volatile organic components of $PM_{2.5}$ particles. After collecting particle concentrates with the BYU PC-BOSS sampler, a GERSTEL Thermo-desorption System (TDS 2) and GERSTEL Cooled Injection System (CIS 3) were used to thermally liberate and isolate the semi-volatile material into a cryogenically cold capillary tube. A section of the tube containing the cryo-focused sample was directly inserted into the ionizer of a low-voltage high-resolution mass spectrometer (LVHRMS).

Table 1. Previously Identified Source Tracer Molecules With Masses Identified in LVHRMS from 4/30/01-5/1/01 PCBOSS Sample

Source Tracers	formula	mass	intensity
Wood smoke:			
guaiacol	$C_7H_8O_2$	124.052	1557
4-methylguaiacol	$C_8H_{10}O_2$	138.068	269
formylguaiacol	$C_8H_8O_3$	152.047	498
4-ethylguaiacol	$C_9H_{12}O_2$	152.084	587
acetylguaiacol	$C_9H_{10}O_3$	166.063	391
4-propylguaiacol	$C_{10}H_{14}O_2$	166.099	85
methylsyringol	$C_9H_{12}O_3$	168.079	611
acetylsyringol	$C_{10}H_{12}O_4$	196.074	531
retene	$C_{18}H_{18}$	234.141	101
Auto exhaust:			
cyclopenta(cd)pyrene	$C_{18}H_{10}$	226.078	1691
benzo(b)fluoranthene	$C_{20}H_{12}$	252.094	29662
benzo(k)fluoranthene	$C_{20}H_{12}$	252.094	29662
Auto brakes:			
triethylene glycol-monomethyl ether	$C_7H_{16}O_4$	164.105	272
triethylene glycol-monoethyl ether	$C_8H_{18}O_4$	178.121	82
Meat cooking:			
decadienal	$C_{10}H_{20}O$	156.151	116
myristic acid	$C_{14}H_{28}O_2$	228.209	353
palmitic acid	$C_{16}H_{32}O_2$	256.24	1634
oleic acid	$C_{18}H_{34}O_2$	282.256	179
stearic acid	$C_{18}H_{36}O_2$	284.272	5870
Tobacco smoke:			
cotinine	$C_{10}H_{12}N_2O$	162.116	343

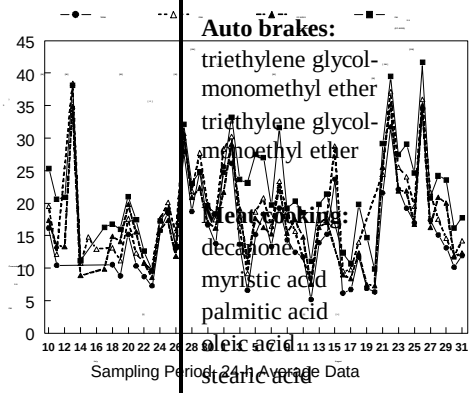

Figure 1. Comparison of 24-h average fine-particulate mass concentrations. The TEOM® monitor was operated at 50°C. The FRM mass is measured by the $PM_{2.5}$ FRM sampler using EPA protocols. PC-BOSS is the continuous non-volatile (Filter Retained) mass calculated from the PC-BOSS determined chemical components. $PM_{2.5}$ is the total fine-particulate mass determined with the PC-BOSS including the semi-volatile nitrate and organic material. Days when the meteorological source of the $PM_{2.5}$ could be identified are also indicated. W is for transport to the NETL site from the west. SW is for transport to the NETL site from the southwest. E for for transport to the NETL site from the east to southeast. L is for locally generated pollutants. The size of the bracket is indicative of the length of the period considered for each meteorological transport condition.

Some preliminary results of the LVHRMS characterization technique are presented in Table 1. These preliminary results and those from a high-resolution gas chromatograpy-mass spectrometry investigation of samples collected and concentrated with this methodology were presented at a recent American Chemical Society meeting. [5] This analysis technique shows promise for the rapid identification of potential Hazardous Air Pollutants (HAPS) in the organic fraction of particles.

SEM/EDX characterization of $PM_{2.5}$ particles

In order to provide information about the degree or extent that coal-fired electric power generating facilities directly contribute to the primary particulate matter load in the Pittsburgh regional ambient air, the number of spherical aluminosilicate (SAS) particles were estimated on a quantitative basis. These particles are a characteristic emission from high temperature coal combustion. The total primary and secondary particle concentration was measured from 24-hour samples collected seasonally at the NETL station, located 10 miles south of Pittsburgh, in a suburban environment. This study provided an objective estimate of the contribution that coal-fired electric power generating stations make to the total particle loading in the air. The information gathered can also be used to estimate the potential impacts that the new National Ambient Air Quality Standards (NAAQS) may have on coal-based power systems.

The SAS particles were identified using scanning electron microscopy / energy dispersive x-ray spectroscopy (SEM/EDX). The method used for this study was a modification of the one described in Eatough et al.[6] Twenty-four-hour samples were collected with the Andersen Instruments RAAS 400 speciation sampler equipped with a 2.5- m inlet system. The samples were collected on palladium coated polycarbonate membrane filters with a 0.4- m pore size and were directly examined as-is by a semi-automated counting technique using an R. J. Lee Instruments Personal SEM.

The goal of this examination was to directly characterize a statistically significant number of particles and particle types, representative of the total particle population, with a combination of characteristic morphology and composition as determined by EDX spectra.

Figure 2 is an example of fine-particles commonly observable in NETL $PM_{2.5}$ samples examined with the SEM/EDX technique.

The methods development portion of this technique continued in FY 2001.

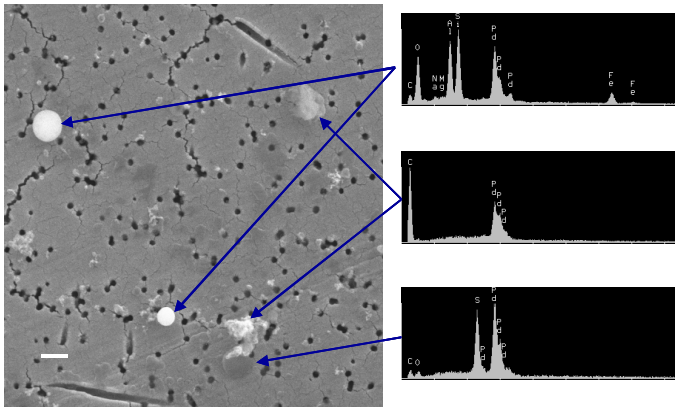

Figure 2. Secondary electron SEM image and EDX particulate spectra.

An application of this method was presented at recent American Chemical Society [7] and International Coal Conference meetings[8].

Critical scientific/business partnerships

Consol Research, the Allegheny County Health Department (ACHD), the R. J. Lee Group, the Mine Safety and Health Administration (MSHA), and Brigham Young University (BYU) are considered partners in the NETL-OST PM $_{2.5}$ project. Consol and NETL share data between Consol's Library Research Center and NETL's ambient air monitoring station. NETL-OST is assisting Consol in implementing its DOE-FE supported Steubenville Comprehensive Air Monitoring Program (SCAMP). Consol and the ACHD co-located their FRM samplers at NETL for several weeks in order to estimate the inter-comparability of the mass data from individual instruments. R. J. Lee continues to provide advice and counsel to the project. The ACHD provided TEOM data from it's numerous stations located throughout Allegheny County. MSHA, under an interagency agreement, continues to weigh NETL samples in their state-of-the-art balance room. NETL maintains an interagency agreement with MSHA to weigh Teflon® filters taken from the EPA-certified FRM sampler. The MSHA balance room meets or exceeds all EPA requirements for the balance room, with the exception that MSHA maintains a different relative humidity in the balance room than that suggested by the EPA. The R. J. Lee Group performed state-of-the-art SEM/EDX analysis on samples of the fine particle matter sampled onto flat polycarbonate filters acquired at the NETL sampling site.

In the summer of FY01, NETL participated with the new EPA supersite at Carnegie Mellon University in a month long regional particulate matter characterization program. Such cooperative seasonal intensive study will continue in FY02.

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